

Izv. Akad. Nauk SSSR Otdel
Khim. Nauk, No. 3, p. 322-326, 1956
Pa-1527

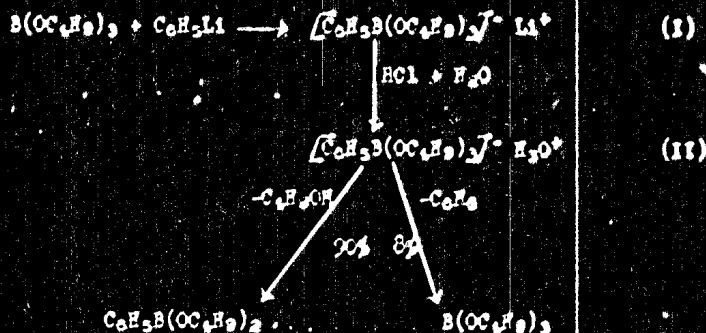
ORGANOBORON COMPOUNDS. V. PREPARATION
OF ISOBUTYL ESTERS OF PHENYLBORIC AND DI-
PHENYL-BORIC ACIDS WITH THE AID OF PHENYLITHIUM

By

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In one of our previous communications¹ we describe the reaction of phenyllithium with isobutyl esters of boric (triisobutyl borate) and of phenylboric acid and formation of complex salts - phenyl triisobutoxy boron lithium and diphenyl-diisobutoxy boron lithium. Further investigation of the above mentioned reactions have shown these reactions to be a method of preparation of phenylboric acid (or its ester) and of ester of diphenylboric acid.

It was found that phenyltriisobutoxy boron lithium (I), upon action of mineral acids, is changed, as expected, into phenylboric acid (or its ester), with an accompanying small yield (8%) of boric acid, or its ester. It is apparent that phenyltriisobutyl borinic (?) acid (II), formed from the lithium salt (I) undergoes further disproportionation with liberation of either alcohol or benzene and the resulting formation of ester of either phenylboric or of boric acids, which then undergo further hydrolysis, as shown in the following scheme:



With the direct treatment of reaction products of phenyllithium and triisobutylborate with hydrochloric acid it is possible to obtain, without isolating salt (I), an 82 percent yield of phenylboric acid. If the reaction mass is treated with anhydrous hydrogen chloride instead, it is possible to obtain a good yield of the diisobutyl ester of phenylboric acid.

¹ B.M. Mikhailov and P.M. Aronovich. D.A.N. SSSR 28 No. 3, 791 (1954).

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The synthesis of arylboric acid esters from trialkyl borates and aryllithium, with the formation of the intermediate borinic (I) acid salt complex suggests that the reaction between alkyl borate esters and organomagnesium compounds may also follow an analogous reaction scheme (mechanism), and is not a metathetical reaction, as it was assumed to be up to now:



It is thus possible to postulate the following scheme for the Grignard synthesis of alkyl substituted esters of boric acid:

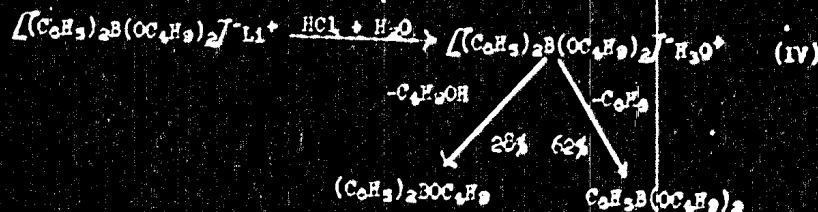


Diphenyldiisobutoxy boron lithium (III) is radically different in its properties from the borinic acid (I) salt complex. The necessary for analysis complex III was prepared in this investigation by addition of lithium isobutyrate to the isobutyl ester of diphenylboric acid, which in turn was prepared from phenylmagnesium bromide and triisobutyl borate:



With this method a good yield of the borinic acid complex (III) is obtained.

Upon action of diluted hydrochloric acid on a water solution of diphenyldiisobutoxy boron lithium (III) a mixture of diphenylboric acid ester (28%) and phenylboric acid is obtained, with a preponderant yield of the latter (62%). Similar results are obtained on hydrolysis, in diluted hydrochloric acid, of the reaction products from phenyllithium and isobutyl ester of phenylboric acid without separation of the intermediate complex (III). In this manner the diphenyldiisobutoxyborinic acid (IV), obtained on acidification, in turn disproportionates, similarly to complex (II), either with liberation of phenol or of benzene, but in this case the formation of benzene is predominant:

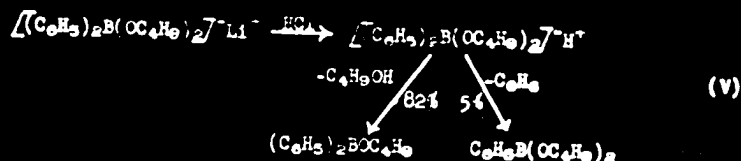


In the phenyltriisobutoxyboronic acid complex (II) the change from one isobutoxy to a phenyl group leads to a profound change in the characteristics and properties of the complex acid. If the phenyl triisobutoxyboronic acid complex (II) disproportionates in full compliance with the effect of the relatively greater electronegativity of the isobutoxy radical, with its greater tendency, as compared to phenyl radical, to split off as an ion, then in case of the diphenyldiisobutoxyboronic acid anion (IV) the less electronegative phenyl radical has a greater tendency to split off.

² B.M. Mikhailov and V. A. Vaver, D.A.N., SSSR 102, 531 (1955).

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In order to study the influence of the medium on the disproportionation of diphenylisobutoxyborinic acid anion. The authors carried out a series of tests on the action of anhydrous hydrogen chloride on the complex salt (III). It was found that in contrast with the results obtained under similar conditions with complex salt (II), the ester of diphenylboric acid is obtained in the 82% yield while only 5% yield of phenylboric acid was reached:



The change of anion in complex ion (IV) for a proton in complex acid V has a profound effect on the character of its disproportionation.

The method of disproportionating the complex salt (III) with anhydrous hydrochloric acid has significance as a preparatory method. Thus if the products of reaction between phenyllithium and the ester of phenylboric acid are treated with anhydrous hydrochloric acid directly, without isolation of the complex salt (III), the ester of diphenylboric acid may be obtained in up to 70 percent yields.

EXPERIMENTAL

Action of Hydrochloric Acid on Phenyltris(isobutoxy)boronlithium

To a solution of 6.28 grams (0.02 moles) of phenyltris(isobutoxy)boronlithium in 10 ml. of water, (the complex salt was obtained by addition of lithium isobutyrate to the diisobutyl ester of phenylboric acid) 5 ml. of 30% hydrochloric acid were added. The resulting mixture was extracted four times with diethyl ether. The combined ether extracts were then distilled to get rid of the diethyl ether solvent.

To the remaining solution 15 ml. of water were added and then the distillation was continued to remove isobutyl alcohol and water. On cooling the residue, the phenylboric acid solids were filtered off and dried. Yield of dry product - 1.97 grams. Another 0.22 grams of phenylboric acid were obtained by extracting the filtrate with diethyl ether and then evaporating off the solvent. Total yield of phenylboric acid product was found to be 90% of theory. The melting point of crude product was 207-210° C.

To the water solution (residue from the second ether extraction after the isobutanol removal step) sufficient aqueous alkali was added to make the resulting solution slightly alkaline and then the solution volume was reduced to less than 10 ml. by evaporation. The residue was treated with 20 ml. methanol, precisely neutralized with acid and then tested with two grams of mercuric chloride. The reaction mass remained neutral indicating the absence of phenylboric acid. It was then titrated for boric acid in presence of mannitol with standard 0.1N alkali. Found 0.097 grams of boric acid, that is 7.8% of theoretical yield.

Phenylboric Acid and Its Isobutyl Ester

A solution of phenyllithium, obtained from 17.5 grams (0.11 moles) of bromobenzene, 1.6 grams of lithium metal, and 175 ml. of diethyl ether, was precooled to -5°C . To the cooled, agitated solution 25 grams (0.1 moles) of triisobutylborate in 50 ml. of diethyl ether were added with continuous additional cooling of the reaction mass. The major portion of the addition of reactants was carried out at -50°C . during the period of 30-40 minutes. The resulting mixture was agitated for 5 hours at -70°C . and then left overnight at that temperature. On the next day the reaction mass was acidified with 20% hydrochloric acid and the ether layer was separated with a separatory funnel. The water layer was treated twice with additional small quantities of diethyl ether.

The combined ether extracts were then distilled to remove the ether solvent. The remaining residue was diluted with 50 ml. of water and then again distilled to remove isobutanol and some water. The resulting cooled slurry was filtered to remove the phenylboric acid product, which was then dried and weighed. A yield of 10 grams, 82% of theoretical, was obtained. The melting point of crude product was $208-212^{\circ}\text{C}$.

In preparation of diisobutyl ester of phenylboric acid, a similar procedure was used. The cooled reaction mass was treated with anhydrous hydrogen chloride in this case, the ether extracts were obtained as above, after which the resulting product was filtered and washed with benzene. The filtrate was further treated by removing isobutanol and benzene by distillation. The residue was fractionally distilled. Total yield was 16 grams (68% theoretical) of the ester product. Boiling point $116-117^{\circ}\text{C}$. at 5 mm.Hg; d_4^{20} 0.9043.

Found:	% $\text{C}_{10}\text{H}_{16}$	32.76;	% B	4.52
$\text{C}_{10}\text{H}_{16}\text{B}(\text{OC}_4\text{H}_9)_2$ (calc.):	% $\text{C}_{10}\text{H}_{16}$	32.95;	% B	4.62

Diphenyldiisobutoxyboronlithium

To 77 ml. (0.1 moles) of 1.5 normal benzene solution of butyllithium, cooled in the ice water bath and kept in the atmosphere of dry nitrogen, 11.5 ml. (0.125 moles) of absolute isobutanol were added with continuous agitation. To the resulting clear solution of lithium isobutylate, cooled in the ice water bath, 26.2 grams (0.11 moles) of isobutyl ester of diphenylboric acid, diluted in 50 ml. of diethyl ether, were added with agitation. The resulting reaction mass was further agitated for 3 hours at 0°C . The solvents were then removed by vacuum distillation, in the dry nitrogen atmosphere, introduced through a capillary tube. When the pot material was concentrated the capillary was raised out of the reaction mass, the nitrogen addition being continued over the pot material. The distillation flask was heated in a steam bath during this operation. After complete removal of solvents the pot residue was mixed with 50 ml. of n-hexane, and then filtered. The solids were washed with 40 ml. of n-hexane and dried in vacuum. Yield of diphenyldiisobutoxyboronlithium - 24.6 grams, or 78 percent of theoretical.

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Found:	$\frac{1}{3}$ Li	2.24;	C_6H_5	48.27;	B	3.32
$(C_6H_5)_2B(OC_4H_9)_2Li$ (calc.):	$\frac{1}{3}$ Li	2.18;	C_6H_5	48.46;	B	3.40

Action of Hydrochloric Acid on Diphenyldiisobutoxyboronlithium

15.9 Grams (0.05 moles) of diphenyldiisobutoxyboronlithium were dissolved in 50 ml. of diethyl ether. Sufficient amount of 20% hydrochloric acid was then added with agitation and cooling in the ice bath to make the resulting slurry acid. The ether layer was separated as before, the water layer was extracted further two times with ether. Ether was then removed by distillation from the combined ether extracts. The residue was then diluted somewhat with water and distilled again to remove isobutanol-water mixture. The residue was then mixed with 20 ml. of isopentane and solids filtered out, washed with small portions of isopentane and then dried in vacuum. Yield 3.2 grams of phenylboric acid. The filtrate was treated as follows: isopentane was removed by vacuum distillation and then the residue was further distilled in vacuum. 3.5 Grams of distilled isobutyl ester of diphenylboric acid were obtained (B.P. 142-145° C. at 6 mm.Hg) which represents 27.6% of theoretical yield. The residue from the ester distillation (0.6 grams) represents additional phenylboric acid. Total yield of phenylboric acid 62.9% of theoretical.

Action of Anhydrous Hydrogen Chloride on Diphenyldiisobutoxyboronlithium

A solution of 15.9 grams (0.05 moles) of diphenyldiisobutoxyboronlithium in 50 ml. of diethyl ether was treated for one hour with anhydrous hydrogen chloride, after which the ether solvent was removed by vacuum. The lithium chloride solids were then filtered off and washed with benzene. Distillation of the filtrate yielded a 10.3 gram fraction boiling at 152-154° C. at 6 mm.Hg. Analysis of this fraction showed it to contain 63% C_6H_5 and 4.11% B. Calculations show the mixture to contain 0.57 gram $C_6H_5B(OC_4H_9)_2$ and 9.73 grams $(C_6H_5)_2B(OC_4H_9)_2$. Thus the yield of diisobutyl ester of phenylboric acid was found to be 4.9% of theoretical, while the yield of isobutyl ester of diphenylboric acid was 41.7% of theoretical.

Action of Phenyllithium on Diisobutyl Ester of Phenylboric Acid

a. Treatment with Hydrochloric Acid

To the ether solution of phenyllithium, prepared from 17.5 grams (0.11 moles) of bromobenzene, 1.6 grams of metallic lithium and 175 ml. of diethyl ether, 23.4 grams (0.1 moles) of diisobutyl ester of phenylboric acid were added under conditions previously described for preparation of phenylboric acid. The resulting clear solution was acidified with 20% hydrochloric acid. After removal of diethyl ether and of isobutanol by distillation, the residue was fractionated under vacuum with the help of a fractionating column. The

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following fractions were obtained: Fraction I (0.9 grams, B.P. 112-115° C. at 6 mm.Hg) was found to be a mixture of diphenyl with a small amount of diisobutyl ester of phenylboric acid; fraction II (2.9 grams, B.P. 117-119° C. at 6 mm.Hg) was found to be the diisobutyl ester of phenylboric acid; fraction III (6.2 grams, B.P. 143-144° C. at 6 mm.Hg) was found to be the isobutyl ester of phenylboric acid). The amount of fraction III obtained (6.2) represents 26.1% of theoretical yield of isobutyl ester of diphenylboric acid. The residue from the fractional distillation (5.8 grams) was found to be phenylboric acid. The combined yield of phenylboric acid and its diisobutyl ester represents 60.2% of theoretical.

b. Treatment with Anhydrous Hydrogen Chloride

The reaction between equimolar quantities of diisobutyl ester of phenylboric acid and of phenyllithium was carried out as previously described. The resulting reaction slurry was saturated with anhydrous hydrogen chloride, the ether removed in vacuum, the lithium chloride solids filtered off and washed with benzene. The combined filtrate and washings were distilled to remove benzene and isobutanol and then further fractionated in vacuum. 1.42 grams of Fraction I, B.P. 152° C. at 8 mm.Hg, and 16.97 grams of Fraction II, B.P. 153-155° C. and 8 mm.Hg, were obtained. The following analytical data were obtained:

Fraction I Found:	%C ₁₀ H ₈	38.60;	B 2.95
Fraction II Found:	%C ₁₀ H ₈	62.99;	B 4.55
C ₁₀ H ₈ B(OC ₄ H ₉) ₂ Calc.:	%C ₁₀ H ₈	32.95;	B 4.62
(C ₁₀ H ₈) ₂ B(OC ₄ H ₉) Calc.:	%C ₁₀ H ₈	64.75;	B 4.54

Calculations showed that fraction I contained 0.1 grams of diisobutyl ester of phenylboric acid and 1.1 grams of isobutyl ester of diphenylboric acid, the remainder (1.91-1.20 gm.) being diphenyl. Fraction II contained 2.8 grams of diisobutyl ester of phenylboric acid 15.75 grams of isobutyl ester of diphenylboric acid. Thus the total yield of diisobutyl ester of phenylboric acid was found to be 1.5 grams or 5.5% of theoretical, while the total yield of isobutyl ester of diphenyl boric acid was 16.9 grams or 71% of theoretical.

All analysis were carried out by the method of Wittig². All operations with phenyllithium were done in the atmosphere of dry nitrogen, while the isolation of the complex salts were carried out under anhydrous conditions.

CONCLUSIONS

1. Treatment of phenyltrisobutoxyboronlithium with hydrochloric acid yields phenylboric acid and a small amount of orthoboric acid.

² G. Wittig, et al., Ann. 569, 110 (1949).

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2. The action of diphenyldiisobutoxyboronlithium with hydrochloric acid yields mainly phenylboric acid and in smaller quantities the isobutyl ester of diphenylboric acid. Treatment of diphenyldiisobutoxyboronlithium with anhydrous hydrogen chloride results in a high yield of the isobutyl ester of diphenylboric acid.
3. Reaction of triisobutyl borate ester with phenyllithium results in the 62 percent yield of phenylboric acid.
4. Reaction of diisobutyl ester of phenylboric acid with phenyllithium with a subsequent treatment of reaction products with anhydrous hydrogen chloride results in a 70 percent yield of the isobutyl ester of diphenylboric acid.

Translated by:
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